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Dimorphism of Silver Bromate

DIMORPHISM OF SILVER BROMATE

BY

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

.....
Samuel Jules Gould

ENTITLED.....
Dimorphism of Silver Bromate

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF.....
Bachelor of Science.

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DIMORPHISM OF SILVER BROMATE

I INTRODUCTION

Polymorphism was first observed by Mitscherlich¹ in the case of sodium phosphate, and later in the case of sulphur. To these two cases, others were soon added, so that today a great number of such substances, both organic and inorganic, have found their way into the literature.

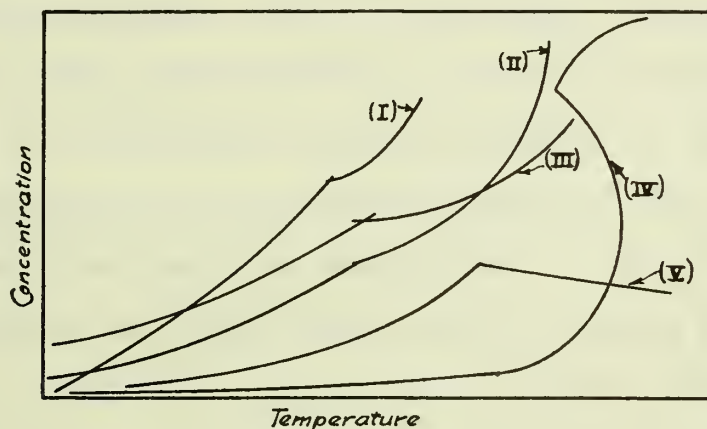
Reedy,² in his work on reaction potentials of silver, discovered that it was impossible to obtain constant potential readings when the cell consisted of a silver anode, a potassium bromate electrolyte, and a platinum cathode. It occurred to him that possibly the variability of his results was due to a dimorphic nature of the silver bromate used. Hence, the work to be explained in this thesis was carried out in order to determine the morphic characteristics of the silver bromate salt.

II HISTORICAL

For the purpose of determining the transition temperature, a choice of a number of methods can be had. The most important of these are: solubility measurements, the dilatometric method, measurements of the vapor pressure, thermometric, optical and electrical methods. All of these, however, are not equally suitable for any given case. It is, therefore, necessary to exercise care in selecting the method most suitable for the purpose. Sometimes, it is possible to employ more than one method, but one

must not expect to obtain identical results from all of the methods used. A difference of several degrees in the values found may quite well occur?

The solubility curve of any substance is continuous, so long as the solid substance in contact with the solution remains unchanged. If any "break" in the direction of the curve occurs, it is an indication that the crystalline structure of the substance under observation has changed, or has reached its transition point. From Figure I, in which the solubility curves of several polymorphous substances are indicated (not, however, drawn to scale), one can readily appreciate how the solubility of these substances vary as their crystalline structure changes. The breaks in the curves occur because every crystalline variety of a substance must have its own solubility.



The substances represented in the graph are as follows: (1) ammonium nitrate⁴ (2) A form of thallium picrate⁵ (3) B form of thallium picrate⁵ (4) benzoic acid⁶ (5) sodium sulphate⁷.

The dilatometric method for determining the temperature of a

transition point makes use of the fact that, in most cases, transformation at the transition point is accompanied by an appreciable change in volume. Consequently, it is only necessary to ascertain the temperature at which this change in volume occurs, in order to determine the transition point. The height of the meniscus of a suitable liquid, which must be without chemical action on the substance under investigation, will indicate by a sudden rise in the capillary where the transformation occurs. This method was used by Van't Hoff⁷ in his determination of the transition point at which sodium sulphate and magnesium sulphate form astracanite.

Both the solubility and dilatometric methods are the ones used in carrying out this work and will be further explained in the course of this paper.

A very important factor to be taken into consideration in a transition point determination is that of suspended transformation of one crystalline form of a salt into the other. These transformations do not necessarily take place immediately as the transition point has been passed; and it has, therefore, been found possible to follow the solubility curve of a given crystalline form beyond the point at which the new form theoretically should appear. This phenomenon which has been encountered in the transition point determination of silver bromate by the solubility method will be discussed in more detail in a later part of this paper.

When two substances have analogous compositions, such as

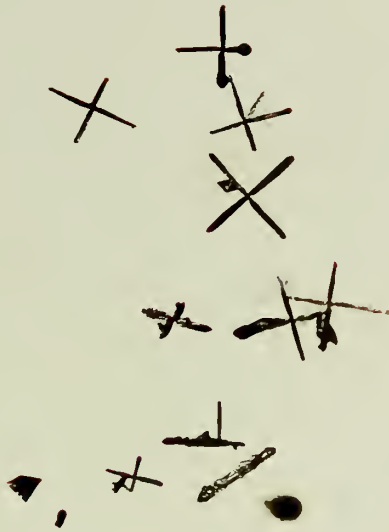
arsenic acid, H_3AsO_4 , and phosphoric acid, H_3PO_4 , their salts form crystals which resemble each other very closely. This phenomenon is so marked that from a solution containing both substances, mixed crystals, that is, homogeneous crystals containing both substances in varying proportions, can be obtained. It is also to be noted that isomorphous compounds possess very similar physical and chemical properties, and it is because of these characteristics that Mitscherlich in 1819 discovered the isomorphism of potassium and sodium phosphates and arsenates.

Retgers⁸ in his work on isomorphism, discovered that silver chlorate crystals existed in two distinct types. He isolated a short quadrangular prism and also a long needle form. Now, according to the rule of Mitscherlich, the analogy of silver chlorate, $AgClO_3$, to silver bromate, $AgBrO_3$, is sufficient hypothesis to imply that silver bromate would also exist in two forms, or that it is dimorphous. This hypothesis was corroborated in the course of this work.

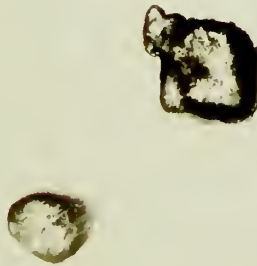
III EXPERIMENTAL

While crystallizing silver bromate from hot solutions, two distinct types of crystals were observed whose contours were apparently identical to those of silver chlorate. The short quadrangular crystals were deposited from solution at a much lower temperature than needle shaped crystals. The two types are represented in Figure II. With this information on hand, procedure was made to determine the transition point of silver bromate.

The silver bromate prepared for this work was made by treating a solution of potassium bromate with an equimolecular amount of

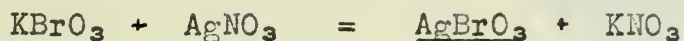


NEEDLE CRYSTALS



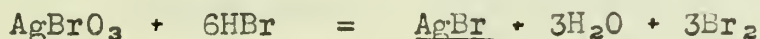
QUADRANGULAR PRISM CRYSTALS

silver nitrate solution and precipitating the silver bromate formed, in the cold.



The apparatus used for its preparation is illustrated in Figure III. The precipitated silver bromate was collected on the filter plate and easily washed free from nitrates.

To determine whether or not the prepared silver bromate was associated with water, a quantitative determination was made of a sample. A weighed amount of the salt was treated with redistilled hydrobromic acid and evaporated to dryness under a hood. The silver bromide residue was weighed and upon calculating back to its equivalent in silver bromate, it was found to be 99.92% pure. The difference of 0.02% is within the accuracy of an analytical determination.

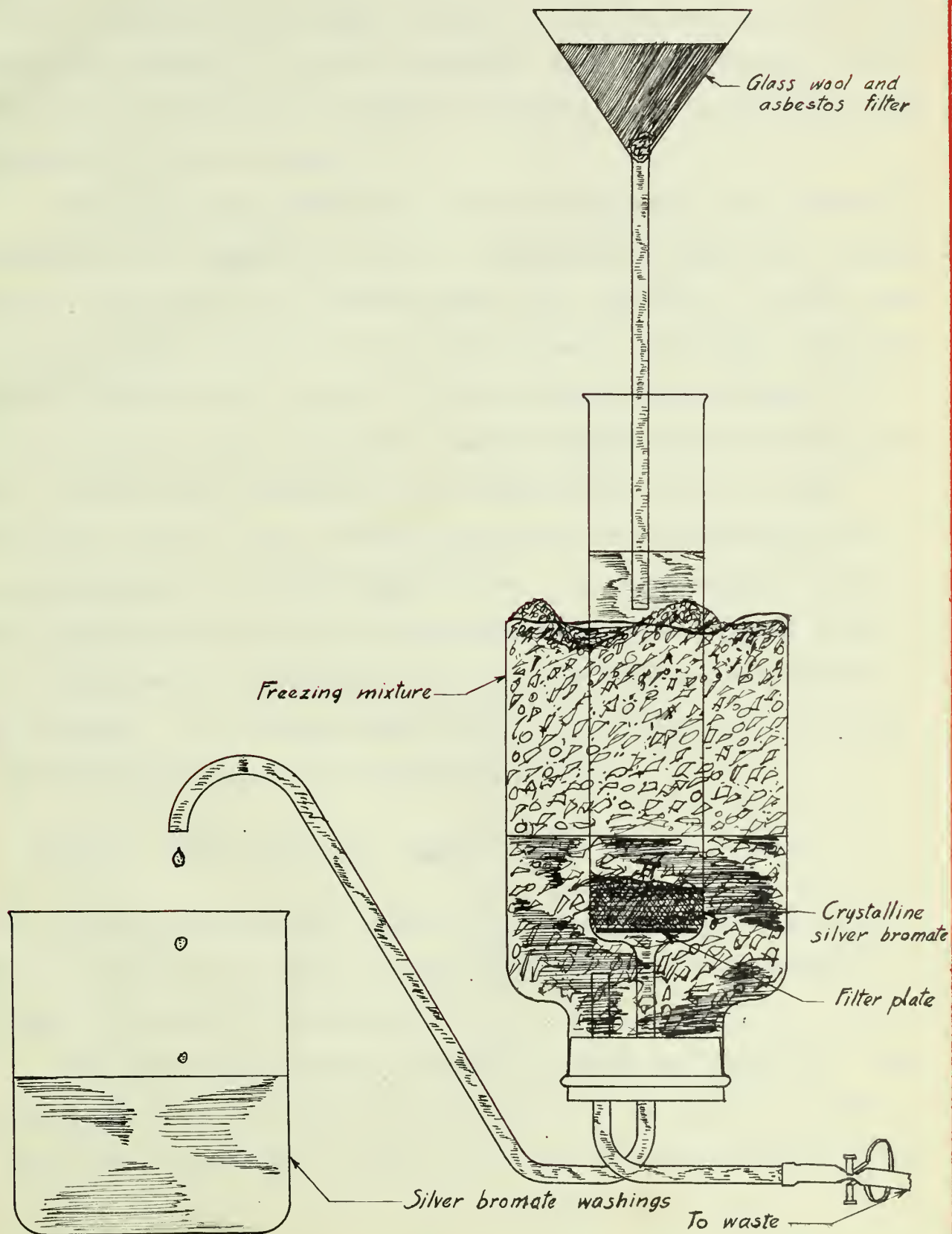


From the analytical results obtained, it was concluded that silver bromate is an anhydrous salt.

It is a well known fact that light is conducive to the reduction of some silver salts, the action being accompanied with a change in color. Böttger² prepared two samples of silver bromate, one which he preserved in a dark bottle and kept in the dark until ready for use, while the other he subjected to the action of light. After a definite period of time, he determined the conductivity of both samples and obtained results that checked

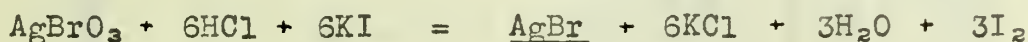
APPARATUS USED IN THE PREPARATION
OF SILVER BROMATE

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almost identically. It is also to be noted that no change in color occurred to the sample exposed to the action of light. From Böttger's results, it can be concluded that silver bromate is unaffected by the action of light; consequently, no precautions were necessary in this respect.

The solubility method was the first employed in an effort to determine the transition point. The apparatus used was a thermostat consisting of an ordinary waste jar, Figure IV, in which was placed a glass vessel for the silver bromate solution. Samples were withdrawn with a pipette at the desired temperatures. A water bath was used, but upon reaching temperatures up near 100° C., it was found desirable to use transformer oil as a bath. Constant stirring and a thermo-regulator were employed for the maintenance of constant temperatures. In every case a sample was maintained at constant temperature for several hours before it was withdrawn for analysis, to insure equilibrium and complete saturation. The samples were analyzed for their silver bromate content according to the following reaction:



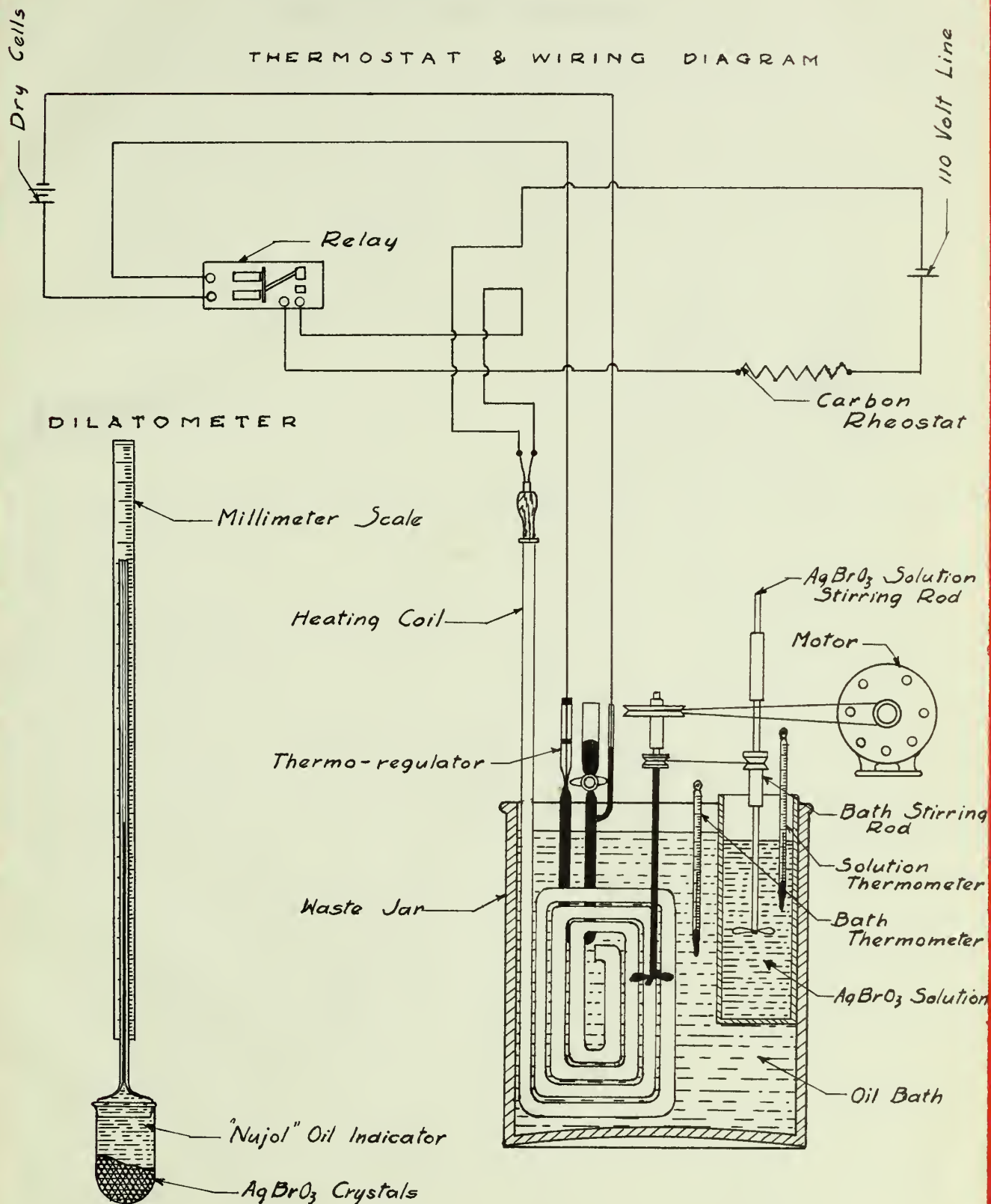
The iodine liberated was titrated with standard sodium thiosulphate solution, and from the data obtained the silver bromate content was easily calculated.

A graph of the results obtained is shown in Figure V. The graph, it is to be noted, is represented in two parts, a black curve and a green one. The black curve represents the solubili-

APPARATUS USED FOR THE DETERMINATION OF THE TRANSITION POINT

9

THERMOSTAT & WIRING DIAGRAM



CURVE OF SOLUBILITY RESULTS IN THE DETERMINATION OF THE TRANSITION POINT OF SILVER BROMATE

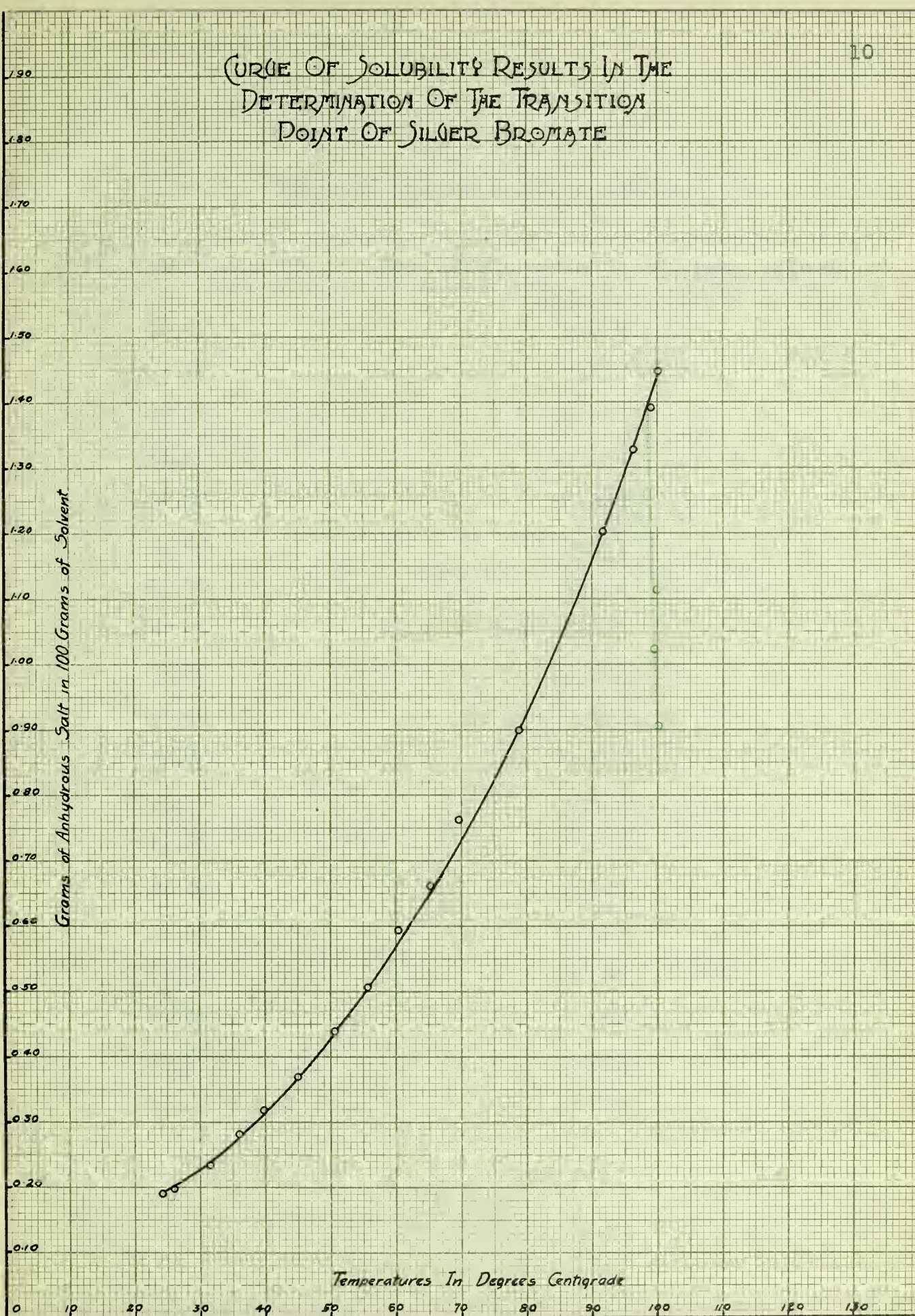


Table of Solubilities of AgBrO_3

Temperatures in °C	Gms. Anhyd. Salt in 100 Gms. Solvent
25.00	0.196
26.90	0.202
32.10	0.241
36.90	0.289
40.50	0.324
45.60	0.377
51.10	0.448
56.10	0.511
60.60	0.601
65.80	0.671
69.90	0.773
78.70	0.910
91.10	1.215
95.90	1.340
98.50	1.405
99.20	1.035
99.50	1.460
99.80	1.125
100.00	0.920

ties from 25.0° C. to 99.7° C., which is the boiling point of a silver bromate saturated solution at 740 millimeters pressure. Duplicate runs were made of all the points on this curve and very good checks were obtained. The green curve contains points which represent the solubilities from the transition point to 100° C. However, these points were not easily duplicated, so that an element of doubt exists as to their accuracy.

As has been explained in the first part of this paper, a suspended transformation is a very common occurrence. The doubt in regard to the green curve is attributed to suspended transformation. The transition point in a case of suspended transformation would appear at a higher temperature, but in the case of silver bromate, the transition point is so close to the boiling point of its solution that a transition could not be hoped for at a higher temperature. But, if the green curve is correct, a transformation can be said to occur at about 98° C.

The solubility values obtained are shown in the table of solubilities. The only data available from the literature on the solubility of silver bromate are four values, all of which are in the neighborhood of 25° C., and are given in the tables of Landolt and Börnstein. Moreover, the solubility method is one that has never been employed before for this work. The values in the literature were all determined by the conductivity method.

To confirm the results obtained by the solubility method, it was decided to determine the transition point by another method. For this work, the dilatometer shown in Figure IV was used. It

consists of a bulb in which the substance under observation was placed, and a long glass capillary stem in which the elevation of the liquid resulting from the expansion of the substance was noted. The scale attached to the glass stem gave the readings in millimeters.

A quantity of silver bromate was placed in the bulb to about one-third of its volume and then filled with Nujol, a saturated paraffin oil of high boiling nature, which is chemically inactive upon the salt. The stem was then fitted into the ground glass mouth of the bulb and due to capillarity the oil rose in it to a desirable height. After fastening the stem securely to the bulb, it was ready to be submerged into the oil bath for readings. The scale and stem which were attached together were supported by clamps from above.

Exceedingly good results were obtained in this determination, as can be seen from the curve in Figure VI. From the curve obtained the transformation occurs at about 99 degrees Centigrade. The points on the curve beyond 104° are unreliable because of gas liberated at that temperature, due to the instability of silver bromate, which decomposes to liberate oxygen.

The results obtained by this method confirm the fact that a suspended transformation of silver bromate occurs in solution, and that the green section of the solubility curve can, in all probability, be considered correct.

CURVE OF DILATOMETER READINGS IN THE
DETERMINATION OF THE TRANSITION
POINT OF SILVER BROMATE

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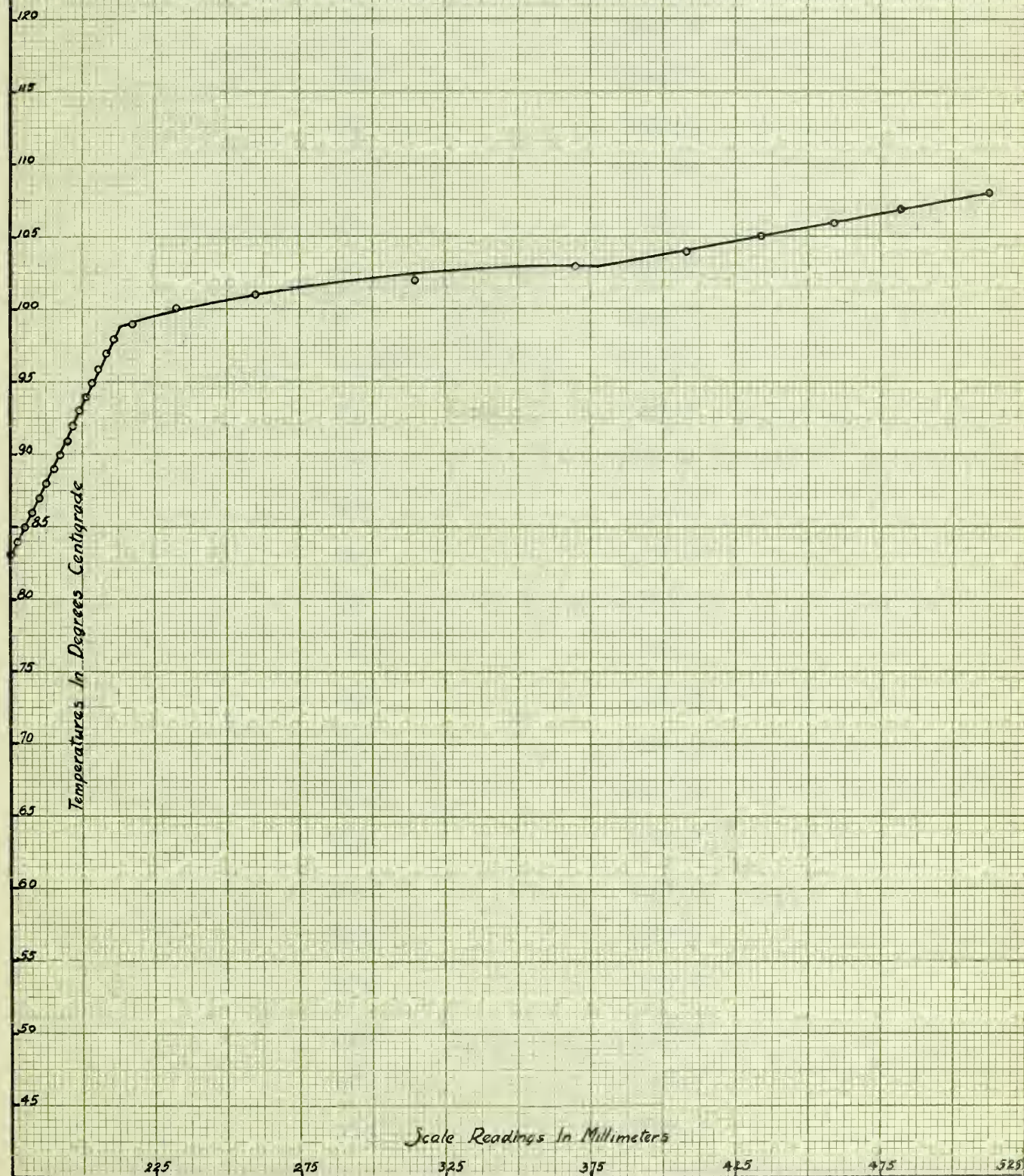


Table of Dilatometer Readings

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Temperature in °C	Scale Readings in mm.
83	175.0
84	177.0
85	180.0
86	182.5
87	185.0
88	187.5
89	190.0
90	192.0
91	194.0
92	196.0
93	199.0
94	201.5
95	203.0
96	205.5
97	207.5
98	210.5
99	217.0
100	232.0
101	265.0
102	315.0
103	370.0
104	408.0
105	433.0
106	459.0
107	482.0
108	512.0

IV SUMMARY

The results of this work show that silver bromate is a dimorphous compound whose crystals are of quite a diverse character. One variety is a short quadrangular prism, while the other possesses a needle shaped form.

The transition point can be fairly accurately determined and is found to be at about 99° C.

The hypothesis which was drawn from the analogy of silver chlorate to silver bromate has been confirmed by this work, and a new field of investigation has been opened for all salts with structures similar to that of silver chlorate.

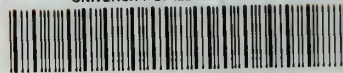
The careful methods followed were instrumental in obtaining a table of solubilities of silver bromate, heretofore unavailable in the literature.

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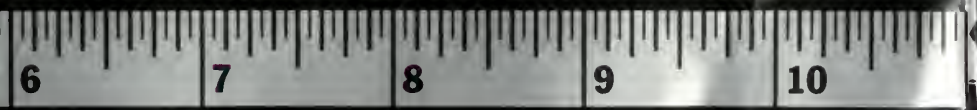
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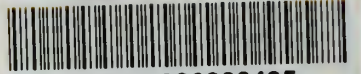
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